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"DIFFUSION OF SMALL MOLECULES IN RADIATION DAMAGED PMMA"

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Ultraviolet irradiation of poly(methyl methacrylate), PMMA, creates radicals which can initiate polymerization of acrylic acid to form block and/or graft copolymer with solubility different from that of PMMA. Selective development of modified PMMA produces negative tone images. The detailed lithographic aspects of this process were investigated in our laboratory. To study further the radiation-induced acrylic acid modification of PMMA, a quartz crystal microbalance was constructed in the reaction chamber and the weight change of PMMA films coated on the quartz crystal was directly monitored during the modification process. The weight of incorporated acrylic acid at a certain reaction time was proportional to the incident dose. With higher dose the increase in weight accelerated as the reaction proceeded. Several solvents of similar boiling points but different solubility parameters were studied in the same way and it was found that those which had solubility parameters similar to PMMA exhibited enhanced diffusion rates after the polymer film had been irradiated. These results suggest that the relaxation of PMMA chains is facilitated by increased free volume in the irradiated polymer film, when the polymer chains respond to swelling stress.					
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Diffusion of Small Molecules in
Radiation Damaged PMMA Thin Films

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Introduction

When an organic polymer is subjected to radiation, the absorbed energy induces chemical changes in the polymer that affect its physical and chemical properties. In positive resists such as poly(methyl methacrylate) (PMMA), main chain scission occurs, resulting in a decrease of molecular weight of the polymer in exposed areas. Selective development of the exposed area depends on the solubility difference between exposed and unexposed areas which mainly comes from molecular weight changes. However, irradiation of polymers leads to the formation of free radicals (and other active intermediates) which are present even at doses much lower than that required to cause a sufficient solubility change. The radicals trapped in the rigid polymer matrix below T_g can be used to initiate polymerization of a monomer to produce a modified copolymer with very different solubility than that of the parent polymer. Gazard et al.(1) reported markedly increased sensitivity of PMMA to electron beam irradiation by adding acrylic acid monomer to irradiated PMMA. The detailed lithographic properties of this process with deep UV, X-ray, proton beam and electron beam were investigated in our laboratory(2). To study further the acrylic acid modification of PMMA, a quartz crystal microbalance was constructed in the reaction chamber. The weight change of PMMA film during the modification and diffusion of several solvents into deep UV irradiated PMMA film was followed with the microbalance.

Experimental

A chlorobenzene solution of PMMA (7% by weight) was spin coated on a 0.5 inch diameter gold coated quartz crystal. The coated PMMA was baked for 30 minutes at 140°C. The PMMA film on the quartz crystal was exposed to deep UV and then placed in the sensor head in the reaction chamber. The reaction vessel was then evacuated to 10^{-6} torr with a diffusion pump. The temperature of the quartz crystal sensor head was controlled by circulating water with a Haake temperature controller bath. Acrylic acid modification was carried out by siphoning degassed monomer into the reaction chamber which was immersed in a water bath at 55°C. The frequency change was recorded at 1 minute intervals. After 30 minutes, the quartz crystal was taken out, rinsed with water and dried in a vacuum oven. In the case of solvent diffusion studies, the reservoir containing degassed solvent was also immersed in a water bath at 55°C. After both chambers were disconnected from the vacuum line, a small fraction of the solvent was directly siphoned into the reaction vessel by opening the valve which separates the reaction chamber and the reservoir and the frequency change was monitored.

Results and Discussion

pected that more acrylic acid should be polymerized at higher doses at a particular reaction time. The data obtained with the quartz crystal microbalance show that the weight of acrylic acid incorporated at a certain reaction time is proportional to the incident dose.

When an irradiated PMMA film is exposed to acrylic acid vapor, the acrylic acid diffuses into the film; 1) the monomer diffuses homogeneously into the film regardless of any differences between the irradiated and the unirradiated areas and is polymerized where radicals are present, or 2) physical and/or chemical changes in the irradiated area of the film can affect the selective diffusion of monomer into the radiation damaged area. Recently selective modification of the irradiated area of photoresists with organometallic vapor such as hexamethyldisilazane (HMDS) has received much attention because the modified resists can be developed by anisotropic plasma etching resulting in high resolution images with high aspect ratios(3,4,5). Mechanism studies of these photoresist systems revealed enhanced diffusion of HMDS into the irradiated areas of the films(6,7). However, the chemistry of each system is different, and different mechanisms for the enhanced diffusion of HMDS were reported. These systems are somewhat complicated by several factors such as a mixture of matrix polymer and photoactive compounds and/or photochemical changes of photoactive compounds or polymer itself.

The major changes in deep UV irradiated PMMA film are decrease of molecular weight (with structure changes at broken chain ends) and increase of free volume due to evolution of volatile byproduct(8). Polymerization of acrylic acid diffused in PMMA film generates a continuous concentration gradient as well as structural and T_g changes which complicate the examination of radiation effects on the diffusion of the monomer. Therefore several model solvents were chosen with consideration of their boiling point and solubility parameter (Table 1). The diffusion in this study was carried at 55°C which is well below the T_g of PMMA. Therefore the diffusion can be considered as Case II diffusion(9). Figure 2 shows absorption of water by PMMA film was not affected by deep UV irradiation up to 2 J/cm². However, the diffusion of propyl alcohol, ethyl ether and 2,2-dimethoxy propane was affected by the radiation. Figure 3 shows the effect of radiation on the diffusion of several solvents into PMMA film. The vertical axis is the increased weight of the PMMA film by enhanced solvent absorption after deep UV irradiation, which is obtained by subtracting the weight of absorbed solvent by unirradiated PMMA film from the solvent weight absorbed by irradiated PMMA film. Each solvent exhibits different radiation effects on its diffusion into PMMA film. Interestingly, absorption of heptane, like water, was not affected by deep UV irradiation. Plotting the increased film weight caused by enhanced solvent absorption after deep UV irradiation versus the solubility parameter of the solvent (Figure 4) revealed that enhancement of diffusion by radiation only occurred with solvents the solubility parameter of which is in a narrow range. It seems that the radiation effect on absorption of solvents by PMMA increases as the solubility parameter of the solvents approaches that of PMMA. These results suggest that the relaxation rate of the PMMA chain is facilitated by increased free volume in the irradiated polymer film when the polymer chains respond to swelling stress. Therefore, acrylic acid (solubility parameter: 12) should diffuse into the irradiated area of PMMA film more rapidly than into the unirradiated area. Solvents such as water and heptane do not interact appreciably with PMMA causing no swelling of the polymer.

Acknowledgement

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Table 1. Solubility Parameter of the Solvent Studied(10).

Solvent	Boiling Point (°C)	Solubility Parameter (cal/cm ³) ^{1/2}
Heptane	98	7.40
Ethyl Ether	35	7.62
2,2-dimethoxy propane	83	7.34*
2-Propanol	82	11.50
1-Propanol	97	11.97
water	100	23.50

*calculated from Small's group contribution parameter but not plotted in Figure 4.

Figure 1. Dose Effect on Acrylic Acid Modification of PMMA. The PMMA film on a quartz crystal was irradiated with deep UV, treated with the vapor above 10% aqueous acrylic acid solution for 30 minutes at 55°C and dried in vacuum 70°C for 24 hours.

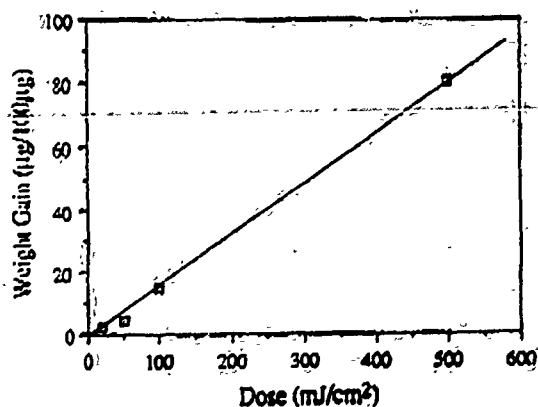


Figure 2. Water Absorption by PMMA Film at 55°C after Deep UV Irradiation.

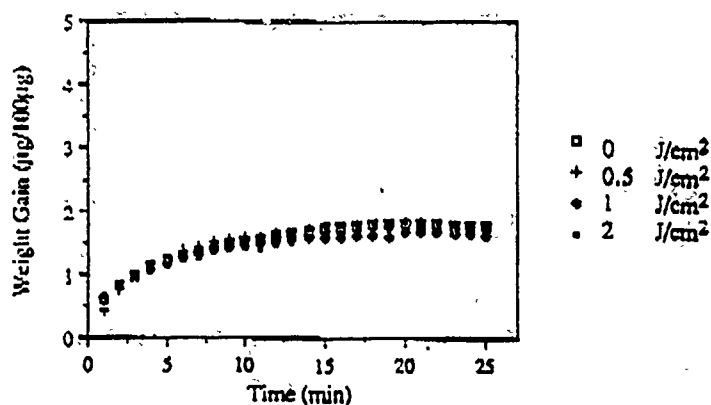


Figure 3. Effect of Deep UV Irradiation on Solvent Absorption by PMMA Film at 55°C at 500 mJ/cm².

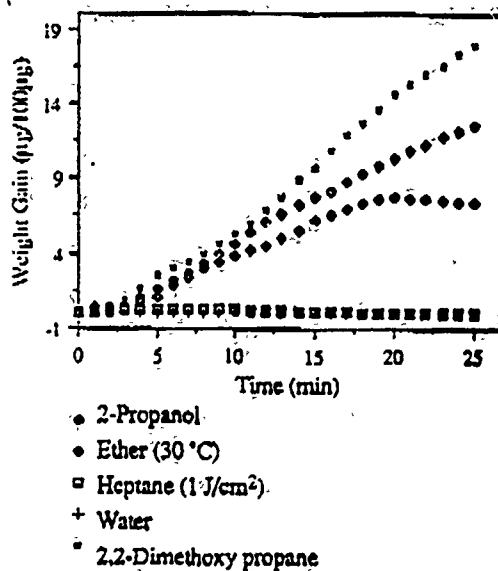
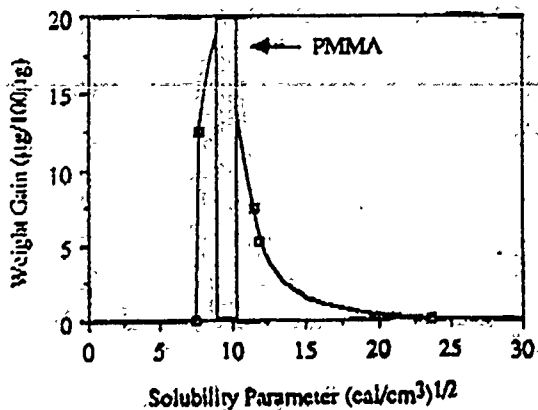


Figure 4. Solubility Parameter versus Increased Weight of PMMA Film by Enhanced Solvent Diffusion at a Deep UV Exposure of 500 mJ/cm².



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